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Mohammadtaghi Vakili

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LIST OF ABBREVIATIONS

Symbol	Description
Aa	Poly acrylic acid
Aam	Poly acrylamide
APTES	3-aminopropyl triethoxysilane
AG25	Acid green 25
BB3	Basic blue 3
BET	Brunauer-Emmett-Teller
COD	Chemical Oxygen Demand
CS	Chitosan
CS/APTES	3-aminopropyl triethoxysilane modified chitosan
CS/HDA	Hexadecylamine modified chitosan
CS/HDA/APTES	Hexadecylamine 3-aminopropyl triethoxysilane modified chitosan
CTAB	Cetyltrimethyl ammonium bromide
DB95	Direct brown 95
DD	degree of de-acetylation
DR23	Direct Red 23
ECH	Epichlorohydrin
EDGE	Ethylene glycol diglycidyl ether
EDX	Energy dispersive X-ray microanalysis
FTIR	Fourier-transformed infrared spectroscopy
GLA	Glutaraldehyde

HDA	Hexadecylamine
M	the molarity of NaOH solution
MB	Methyl blue
MG	Malachite green
MO	Methyl orange
PBMA	Poly(butyl methacrylate)
PEI	Poly ethylene mine
PEMA	Poly(ethyl methacrylate)
PHMA	Poly(hexyl methacrylate)
PMMA	Poly(methyl methacrylate)
RB	Remazol blue RN
RBBR	Remazol brill blue R
RB4	Reactive blue 4
RB5	Reactive black 5
RB81	Reactive blue 81
RBM	Reactive black M-2R
rpm	Rotation per minute
RR	Remazol red3BS
RR222	Reactive red 222
RR3	Reactive red 3
RYG3RS	Remazol yellow gelb 3RS
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscope
TPP	Tripolyphosphate

LIST OF SYMBOLS

Symbol	Description	Units
A_{RP}	Redlich-Peterson isotherm model constant	L/g
b	Langmuir constant	L/g
b_T	Temkin constant related to the heat of adsorption	J/mol
B_{RP}	Redlich-Peterson isotherm model constant	$(L/mg)^g$
C_0	Initial dye concentration	mg/L
C_t	Dye concentration at time t	mg/L
C_e	Dye concentration at equilibrium	mg/L
g	Redlich-Peterson model component	-
ΔG	Gibbs free energy	kj/mol
ΔH	Enthalpy change	kj/mol
K_1	Pseudo first-order constant rate	g/mg/min
K_2	Pseudo second-order constant rate	g/mg/min
K_F	Freundlich constant	$((mg/g)(L/mg)^{1/n})$
K_L	Standard thermodynamic equilibrium constant	L/g
K_T	Temkin constant related to equilibrium binding energy	L/mg
LC50	Lethal concentration required to kill 50% of the population	mg/L
LD50	Individual dose required to kill 50 percent of a population of test animals	mg/kg

n	Adsorption intensity related to Freundlich isotherm	-
p	Denotes the number of experimental data	-
q_e	Adsorption capacity at equilibrium	mg/g
q_m	Monolayer adsorption capacity related to Langmuir constant	mg/g
q_{cal}	Calculated adsorption capacity	mg/g
q_t	Adsorption uptake at time t	mg/g
q_{exp}	Experimental adsorption capacity	mg/g
R	Universal gas constant	J/mol K
R^2	Correlation coefficient	-
R_L	The dimensionless separation factor	
ΔS	Entropy change	kJ/mol
T	Absolute temperature	K
V	Volume of dye solution	L
W	Weight of adsorbent	g
X^2	Chi-square	-
λ_{max}	Maximum wavelenth	nm

PENJERAPAN PENCELUP REAKTIF MENGGUNAKAN MANIK KITOSAN TERUBAHSUAI DENGAN HEKSADESILAMINA DAN 3-AMINOPROPIL TRIETOKSISIALNA

ABSTRAK

Industri tekstil telah mengalami pertumbuhan pesat dalam tahun-tahun kebelakangan ini. Dalam industri ini, pelbagai jenis pewarna telah digunakan untuk tujuan mewarna. Akibatnya, air sisa industri ini mengandungi sejumlah besar warna dan sebatian toksik yang akan memudaratkan alam sekitar jika tidak dirawat. Oleh itu, kumbahan tekstil mempunyai keperluan untuk dirawat dengan kaedah yang cekap sebelum dilepaskan ke saliran air. Di antara semua kaedah rawatan, proses penjerapan didapati sebagai kaedah yang berkesan. Kitosan (CS) merupakan salah satu polimer tabii jadi yang boleh didapati secara meluas. CS telah terbukti sebagai penjerap warna yang berkesan kerana sifat-sifatnya seperti mudah untuk biodegradasi, ciri kationik dan harga yang rendah. Walau bagaimanapun, CS mentah mempunyai ciri-ciri yang mengehadkan prestasi penjerapan seperti kawasan permukaan dan kapasiti penjerapan yang rendah. Oleh itu, CS perlu diubah suai sebelum digunakan sebagai penjerap. Dalam kajian ini, CS telah diubah suai dari segi fizikal dan kimia dan kemudian telah digunakan sebagai penjerap pewarna reaktif (reaktif biru 4 (RB4) dan reaktif hitam 5 (RB5)) dan untuk air sisa tekstil sebenar. Untuk pengubahsuaian secara fizikal, CS telah berjaya ditukar kepada

manik CS. Kemudian, manik-manik CS telah diubahsuai secara kimia menggunakan heksadesilamina (HDA) dan 3-aminopropil trietoksisilana (APTES). Ciri-ciri fizikokimia bagi semua manik CS yang diubahsuai dan tidak diubah suai telah dinilai menerusi kaedah Fourier transformasi spektroskopi inframerah (FTIR), imbasan elektron mikroskopi (SEM), ukuran penjerapan-penyaherapan nitrogen spektroskopi, tenaga serakan X-ray (EDX) dan pengukuran potensi Zeta. Luas permukaan BET bagi manik yang disediakan adalah dalam julat di antara 0.29 dan 1.32 m^2/g. Kesan pH (2-10), suhu (30-50 °C), masa sentuhan, kepekatan pewarna permulaan (50-500 mg/L) dan dos penjerap (0.25-1.5 g/L) telah disiasat. Kapasiti penjerapan maksimum manik CS selepas pengubahsuaian menggunakan HDA dan APTES meningkat daripada 317.1 mg/g ke 433.8 mg/g, 454.7 mg/g dan 468.8 mg /g pada pH 4 dan 30 ° C untuk CS/APTES, CS/HDA dan manik CS/HDA/APTES masing-masing. Data penjerapan dinilai berdasarkan garisan sesuhu keseimbangan penjerapan (Langmuir, Freundlich, Temkin dan Redlich-Peterson), model kinetik penjerapan (tertib pseudo pertama dan pseudo-kedua) dan kajian termodinamik. Untuk semua penjerapan, data isoterma didapati mematuhi model Freundlich dan kajian kinetik menunjukkan bahawa model kadar pseudo-tertib kedua adalah lebih sesuai untuk dipadankan dengan data kaji uji. Nilai negatif parameter termodinamik yakni ΔG^0 (−2.28, −4.70, −2.12 dan −6.64 kJ/mol pada 30 ±2 °C), ΔH^0 (−172.18, −43.82, −101.62 dan −74.32 kJ/mol) dan ΔS^0 (−560.71, −129.08, −314.58 dan −223.35 J/molK) manik manik CS, APTES, HDA dan CS/HDA/APTES masing-masing menunjukkan bahawa proses penjerapan RB4 adalan spontan dan eksotermik. Keputusan yang diperolehi daripada penjanaan semula CS menunjukkan bahawa semua penjerap yang disediakan dapat digunakan beberapa kali dalam kitaran penjerapan dan penyahjerapan. Manik CS diubahsuai dengan kedua-dua HDA dan APTES (manik CS/HDA/APTES) telah

dipilih untuk dinilai bagi penyingkiran RB5 dan rawatan air sisa tekstil sebenar. Keputusan menunjukkan bahawa manik CS/HDA/APTES dapat menyingkirkan 92.1% daripada RB5 dan 93.2% daripada pewarna dalam air sisa tersebut.

ADSORPTION OF REACTIVE DYES BY HEXADECYLAMINE AND 3-AMINOPROPYL TRIETHOXYSILANE MODIFIED CHITOSAN BEADS

ABSTRACT

Textile industry has experienced exponential growth in recent years. In these industries, many different types of dye are being used for coloring purposes. As a result, the effluent of these industries contains large amount of color and toxic compounds. These colors and toxic compounds would be detrimental to the environment if they are left untreated. As such, the textile effluent has a dye need to be treated with an efficient method before being released into water bodies. Among all treatments, adsorption process is found to be an effective method for industrial effluents treatment. Chitosan (CS) is one of abundantly available natural polymers and is an effective adsorbent due to its specific adsorption properties such as biodegradability, cationicity and low price. However, the raw CS suffers from some draw backs such as low surface area and low adsorption capacity which limit its adsorption performance. Therefore, it is necessary for CS to be modified prior to its use as an adsorbent. In the present study CS, was modified physically and chemically and then applied for adsorption of reactive dyes (reactive blue 4 (RB4) and reactive black 5(RB5)) and real textile wastewater. For physical modification, the CS powder was successfully converted to CS beads. Afterwards, the CS beads were chemically modified using hexadecylamine (HDA) and 3-aminopropyl triethoxysilane (APTES).

The physicochemical properties of all prepared modified and unmodified CS beads were characterized by means of Fourier transformed infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), nitrogen adsorption-desorption measurement, energy dispersive X-ray spectroscopy (EDX) and Zeta potential measurement. The BET surface areas of the prepared beads were in the range of 0.29 - 1.32 m^2/g. Effects of pH (2-10), temperature (30-50 °C), contact time (5 to 480 min), initial dye concentration (50-500 mg/L) and adsorbent dosage (0.25-1.5 g/L) on adsorption performance of adsorbents were investigated. The maximum adsorption capacity of CS beads after modification using HDA and APTES increased from 317.1 mg/g to 433.8 mg/g, 454.7 mg/g and 468.8 mg/g at pH 4 and 30 °C for CS/APTES, CS/HDA and CS/HDA/APTES beads, respectively. This could be attributed to the presence of more cationic functional groups on the surface of modified adsorbents which resulted in an increase in the surface charge and enhance dye adsorption performance of adsorbents. The obtained adsorption data were assessed based on equilibrium adsorption isotherms, kinetics adsorption models and thermodynamic studies. For all adsorbents, the isotherm data were significantly described by Freundlich model. The kinetic study revealed that the pseudo-second-order rate model was in better agreement with the experimental data. The negative values of the thermodynamic parameters, including ΔG^0 (−2.28, −4.70, −2.12 and −6.64 kJ/mol at 30 ±2 °C), ΔH^0 (−172.18, −43.82, −101.62 and −74.32 kJ/mol) and ΔS^0 (−560.71, −129.08, −314.58 and −223.35 J/molK) for CS beads and APTES, HDA and HDA/APTES modified beads, respectively, showed that RB4 adsorption is a spontaneous and exothermic process. Obtained results from regeneration studies showed that all prepared adsorbents were able to be used 13 times in the adsorption and desorption cycles. The CS beads modified with both HDA and APTES (CS/HDA/APTES beads) were

selected to be evaluated for RB5 removal and textile wastewater treatment as well. Results showed that CS/HDA/APTES beads were able to remove 92.1% of RB5 and 93.2% of dye in textile wastewater.

CHAPTER ONE
INTRODUCTION

1.1 Water and textile effluent

Water is a vital substance for survival of life and health on earth. About 55% of human body, 65% of animal's tissue and 60% of plants are composed of water. Although more than 70 percent of Earth's surface is covered by water but many people suffer from a shortage of potable water, because most of the existing water on Earth is saline water in oceans which cannot be used for drinking, cooking, farming and industrial activities. The amount of available fresh water on the Earth is very limited and only one percent of the total existing water on Earth is freshwater (Inglezakis and Poulopoulos, 2006). In recent decades, increasing in the world's population, unplanned urbanization, industrialization, agricultural activities, and expanded use of chemicals, have contributed to environmental contamination via emission of wastes and pollutants (Gupta and Suhas, 2009). Inorganic and organic wastes produced by human activities have resulted in high volumes of contaminated water, contamination of limited fresh water resources and thus threaten human health and other living organisms (Dixit et al., 2014).

Malaysia is one of the fastest growing economies in the Asian region where industries such as textile, palm oil, food, rubber, and agricultural industries, play an important role in economic growth (Mallak et al., 2014). In recent years, after the electronic and the palm oil industries, textile industry has flourished and become one of the main sources of income for Malaysia ($5.4 million in 2007). About 1500 textile factories in this country are producing different types of textile products,

playing a positive role in the economic development of Malaysia (Siddiqui et al., 2011). In addition to the textile industry, dyes also are extensively applied by other dyeing industries such as paper, rubber, plastic, food or leather for the production of colored products. In spite of immense economic benefits of these industries for this country, the large volume of produced colored wastewater from these industries are the main sources of industrial wastewater which cannot be ignored by environmental regulations in Malaysia (Lim et al., 2010). About 22% of the total volume of industrial wastewater is due to textile wastewater (Idris et al., 2007).

The wastewater generated by the textile industry, having high salinity, high chemical oxygen demand (COD) concentrations, high temperature, high fluctuation in pH (2–12) and strong coloration is one of the most important environmental concerns (El-Mekkawi and Galal, 2013). Some of the used dyes in this industy directly or during the dyeing process are released to effluents. In the dyeing process, due to the low level of dye-fiber fixation, about 10–15% of the used dyes are lost in wastewater. Eventually, a highly colored wastewater is generated and finds its way to the environment. The release of dyes as wastewater is problematic because of high visibility, resistance, and toxic impact of the dyes (Demirbas, 2009; Ali et al., 2009).

1.2 Textile dyes

The dye is defined as a colored chemical organic compound used for imparting and providing color to other substances (Yagub et al., 2014). The dyes can bind to surface of other materials by mechanical retention, physical adsorption, forming covalent bond or complexes with salts or metals (Chequer et al., 2013). Dyes can be classified according to their chemical structure. There are two major components in a

dye molecule. The first group includes chromophores such as quinoid, carbonyl (–C=O), azo (–N=N–), nitro ($–NO_2$), and methine (–CH=) groups. The second type of components are auxochromes such as hydroxyl (–OH), amine ($–NH_3$), sulfonate ($–SO_3H$) and carboxyl (–COOH) groups (dos Santos et al., 2007). The chromophores are responsible to impart color to the dye and auxochromes are used as a supplement of chromophores to deepen the color and enhance the dye attachment towards the fibers. It should be noted that the sulfonate groups confer very high aqueous solubility to the dyes (Bafana et al., 2011). The ability to adsorb light in the visible region is a feature of all dyes (Asgher, 2012). The structural diversity of dyes made them possible to be classified in several ways such as chemical structure, application class and their solubility. However, the classification based on their usage is the most common method and they can be divided into anionic (acid, reactive and direct dyes), cationic (basic dyes), and non-ionic (dispersed dyes) (Yagub et al., 2014).

Anionic dyes normally have similar characteristics e.g. negative charge, ionic substituent, high water solubility and contain sulphonate (SO_3Na) group but possess dissimilar structure characteristics such as xanthenes, anthraquinone, azonic, and triphenylmethane which increase the dyes resistance to degradation (Tripathi, 2013). Anionic dyes are extensively used in dyeing of polyamide and protein materials (acid dyes) and cellulosic substances (reactive and direct dyes) (Gowri et al., 2014). The process of dyeing is frequently carried out in acidic conditions due to the interaction between protonated amino groups in fibers and negatively charged sulfonate groups of anionic dyes structure in acidic solution (Tehrani-Bagha and Holmberg, 2013).

The positively charged dyes, however, are known as cationic or basic dyes (Tripathi, 2013). Transformation of amino ($–NH_2$) to ammonium ($–NH_3$) groups is

the responsible for their basic and positive properties. This class of dye is widely used for acrylic fibers dyeing due to the negative charge of these fibers, which interact with the positively charged dye molecules (Tehrani-Bagha and Holmberg, 2013). The presence of these functional groups in cationic dyes makes them more water soluble and provides more visibility, brilliance and intensity of colors (Salleh et al., 2011). The term non-ionic refers to the other groups of dye (disperse dye) with small, planar and not ionized molecules (free from ionizing groups). Due to the hydrophobic properties of disperse dyes (limited water solubility and presence of polar groups such as $–NO_2$ and –CN), they are more suitable for dyeing the hydrophobic fibers such as nylon, polyamide, polyester and polyurethane (Uliana et al., 2013; Adinew, 2013).

1.3 Reactive dyes

Reactive dyes was discovered in 1954 and later in 1956 it entered into the commercial market (Kanetkar, 2010). Afterward, due to the favorable dyeing properties, this class of dyes has become one of the most popular and extensively applied dyes for dyeing the cellulosic substrate such as polyamides, wool and cotton (Rizk et al., 2015). These kinds of dyes are called reactive dyes due to the presence of reactive groups on dye molecules and capability of chemically interaction (covalent bonds) with functional groups of fiber (Soleimani-Gorgani and Taylor, 2006).

Reactive dyes represent an increasing market share, (about 20–30%) of the total market for dyes because they are used to dye cotton which makes up about half of the worlds fibre consumption. High popularity of reactive dyes is based on

producing brilliant and fast colors with a wide range of shades using various environmentally friendly procedures. Reactive dyes stand out from other dyes by their ability to make covalent bonds between carbon atoms of dye reactive group and oxygen atoms of cotton hydroxyl groups under alkaline conditions. On the other hand, they suffer from some drawbacks such as high cost of dye, long time for batch processing, high salt content of the wastewater, low adsorption ability, non-biodegradability, high water solubility and low degree of fixation on the surfaces which resulted in generating highly colored wastewater (Nabil et al., 2014). A large fraction, typically around 30%, of the applied reactive dye, is wasted because of dye hydrolysis in the alkaline dyebath (Papić et al., 2004). Among textile effluents, reactive dyes are hardly eliminated under aerobic conditions and are probably decomposed into carcinogenic aromatic amines under anaerobic conditions. Furthermore, it is difficult to remove reactive dyes using chemical coagulation due to the dyes' high solubility in water (Sakkayawong et al., 2005).

Reactive dyes are colored compound which contains one or two groups capable of forming covalent bonds between a carbon or phosphorus atom of the dye ion or molecule and an oxygen, nitrogen or sulfur atom of a hydroxyl, an amino or mercepto group, respectively, of the substrate. Reactive dyes are characterized by azo-based chromophores with aromatic structure combined with various types of reactive groups such as chlorotriazine, vinyl sulfone, difluorochloropyrimidine and trichloropyrimidine (Aksu et al., 2007).

The other difference of reactive dyes with other dyes is in the dyeing process. The anionic properties of both reactive dyes and cellulose, reduce the interaction between them, so the dyeing process is usually conducted in highly concentrated

alkaline conditions (pH 9–12), salt concentrations of 40 g/L to 100 g/L and at high temperatures ranging from 30 °C to 70 °C (dos Santos et al., 2007). However, in the presence of water, some of the dye molecules do not attach to the surface of fiber. This is due to the hydrolysis of their reactive group with the hydroxyl group of water. Consequently, high amount of applied reactive dye is wasted and discharged in the effluent (Patel et al., 2014). The presence of this dye in environment can threat the ecosystem due to its toxic effects and sunlight transmission reduction through aquatic environment.

Reactive blue 4 (RB4) is an important dye which is widely used in the textile industry for coloring of cellulosic fabrics. The release of effluents containing RB4 into the environment without any treatment is a source of public concern. Its health risk is considered to be low due to the presence of low concentration of RB4 in environment. Nevertheless, presence of high concentration of RB4 in environment is toxic. According to the Epolito et al. (2005) the estimated LD50 value for rodent and LC50 value for fish are reported to be 8980 mg/kg of body weight and 1500 mg/L, respectively. These values however, are much higher than the RB4 concentrations in the environment.

RB4 has an anthraquinone molecular structure. Thus, due to its aromatic structure, RB4 molecule has high resistant to biodegradation and can remain stable and colored for a long time (Fanchiang and Tseng, 2009). Its slow environmental degradation is reported to be 0.053 day in air, 150 days in water and soil and 600 days in sediment (Ullhyan, 2014; Epolito et al., 2005). The presence of RB4 in water bodies leads to aesthetics problem and affects the aquatic ecosystem by adsorbing, reflecting and reducing the sunlight transmission through aquatic environment.

Therefore, this can lead to complications in the environment if the effluent is discharged without suitable treatment for dye elimination.

1.4 Textile effluent treatment

In the recent years, rapid expansion of the industry has led to an increase in industrial effluents. This is considered as one of the main environmental and water pollution sources. Textile effluents constitute a major part of industrial wastewater. The release of dyes to the environment through untreated wastewater poses serious threat to the freshwater sources, aquatic life and human beings (Sathian et al., 2014). Hence, given the importance of water for human life, an effective method for treatment of dyes wastewater is necessary to control water pollution in many countries.

Various conventional methods such as coagulation (Wei et al., 2015), membrane filtration (Chen et al., 2015), flocculation (Fu et al., 2015), electro chemical oxidation (Chatzisymeon et al., 2006), Fenton processes (Bae et al., 2015), photochemical oxidation (Modirshahla et al., 2011) and ozonation (Turhan et al., 2012) have been applied for the removal of dyes from contaminated waters and industrial effluents. However, these methods usually suffer from their high cost, low efficiency, long processing period or secondary pollution (Liu et al., 2013a). Among all treatment methods, adsorption process is found to be as an effective and economical method for treating industrial effluents (Qiu et al., 2009).

Different materials have been applied as adsorbents for removal of dyes. Chitosan has been gaining a lot of attention by researchers for use as an adsorbent for dye removal. It is a deacetylated form of chitin and the second most abundant

polymer in the world after cellulose. In addition, this biopolymer has many specific properties such as the presence of different adsorption sites on chitosan chain, biodegradability, cationicity, high adsorption capacity, macromolecular structure, abundance and low price (Sadeghi-Kiakhani et al., 2013). Thus, there has been a growing interest on the use of chitosan as adsorbent in adsorption process for removal of dyes. Different types of modification agent can be used to improve the adsorption performance of chitosan based adsorbent by introducing new functional groups. This area can open a new window in preparation of low-cost, environmental friendly adsorbents based on renewable biomaterial.

1.5 Problem statement

Today, the world is witnessing significant technological progress to provide a better life for mankind. These technological processes have their own negative impacts on ecosystem and lead to contamination of the environment. Malaysia has various industries such as textile, palm oil, food, rubber, and agricultural industries. Among them the textile industry is one of the most important industries in Malaysia (Lim et al., 2010). In terms of environmental pollution, textile industry is one of the leading and effective industries due to large consumption of water and dyes and consequently generating massive amounts of colored effluent (Nawaz and Ahsan, 2014). The presence of dyes in effluent leads to unpleasing conditions in water bodies by affecting the dissolved oxygen content , water transparency and aesthetic merit as well as endangering the aquatic flora and fauna due to their toxicity, high water solubility, non-biodegradability and stability (Duarte et al., 2013). Therefore,

it is important to minimize aforementioned dyes negative aspects by effectively eliminating them.

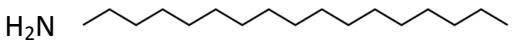
Among all treatment strategies, adsorption process by using efficient adsorbents has been shown to be an effective method for the elimination of dyes from wastewater because they are rapid, convenient and impermeable to toxic contaminants. Hence, many efforts have been carried out in the recent years in order to produce more cost effective alternative adsorbents with effective adsorption capacity that can be used in dye wastewater treatment. Recently researchers have been focusing on utilization of adsorbents composed of natural polymers that are not harmful to the environment and also can be obtained in abundance especially polysaccharides such as chitosan (Crini and Badot, 2008).

Chitosan is an abundantly available low-cost bio-polymer for dye removal that can be obtained from natural resources. It has received a lot of focus due to its specific properties such as biodegradability, biocompatibility, nontoxicity, antibacterial property, cationicity, high adsorption capacity, macromolecular structure, hydrophilicity, abundance and low price (Muzzarelli et al., 2012). Based on the above properties, chitosan potentially has high affinity to adsorb dyes due to several functional groups available on this material. Beside all of these advantages, the raw chitosan in the form of flakes suffers from some draw backs such as its low acid stability, low surface area, low porosity and low adsorption capacity, which limit its adsorption performance. Therefore, modification of chitosan (chemically and physically) could be an effective solution to produce a product with the desired properties to overcome the limitations of chitosan. Raw chitosan can be modified physically by conversion of raw chitosan flakes into beads. Compared with chitosan

flakes, the use of chitosan in the form of beads presents better adsorption properties due to its higher specific surface area. Afterward, increasing the amount of functional groups through chemical modification brings new derivatives with improved adsorption properties.

This study is aimed at preparing the physically and chemically modified chitosan beads. The chitosan physically modified by conversion into the beads form and then were chemically modified by two chemicals i.e. Hexadecylamine (HDA) and 3-aminopropyl triethoxysilane (APTES) to obtain new adsorbents with more amino groups. HDA and APTES can be used to modify chitosan properties and enhance the adsorption performance of CS. Molecular structures of HDA and APTES are shown in Figure 1.1. HDA as a cationic surfactant and APTES as a cationic amine-terminated organosilicon with a hydrophilic group (NH_2) can be used with the hope of increasing the amino groups onto the surface of chitosan as well as enhancing the cationicity and adsorptive capacity of chitosan for removal of dyes from aqueous solutions. The developed adsorbents can be used as suitable adsorbents for removal of reactive dyes, reactive blue 4 and reactive black 5, from aqueous solution through batch adsorption process. Reactive dyes are anionic dyes normally have similar characteristics e.g. negative charge, ionic substituent, low adsorption capability, high water solubility and contain sulphonate (SO_3Na) group. Therefore, using suitable adsorbents with positive surface charge and high cationicity is an appropriate method for elimination of reactive dyes from aqueous solutions.

(a)



(b)

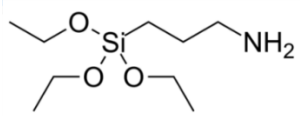


Figure 1.1: Molecular structure of (a) HDA and (b) APTES.

1.6 Research objectives

The aim of the current study is to achieve the following objectives:

- To prepare and characterize the modified chitosan beads for correlation between the preparation conditions such as temperature, concentration and time on dye removal.
- To determine the effect of adsorption parameters including adsorbent dosage, initial dye concentration, initial pH, time and temperature on adsorption of reactive dye in adsorption process.
- To determine the isotherms, kinetics and thermodynamics of batch adsorption process using the prepared adsorbents.
- To evaluate the efficiency of the modified adsorbents in dye removal and COD reduction of real textile wastewater.
- To determine the regeneration of the adsorbents of reactive dye after several times repeated cycle of adsorption and desorption.

1.7 Scope of the study

The current research focuses on the adsorption of reactive dyes on modified chitosan beads. This research also involves investigation on utilization of HDA and APTES as new modification agents on chitosan beads. Fourier transformed infrared spectroscopy (FTIR), surface area and porosity distribution, scanning electron microscope (SEM) and Zeta potential were used to investigate and clarify the physicochemical changes after modification of the beads. The efficiency of the prepared modified adsorbents was tested for adsorption of reactive blue 4 (RB4) and reactive black 5 (RB5) dyes in the batch adsorption system. Moreover, adsorption parameters such as adsorbent dosage, initial dye concentration, initial pH, time and temperature were evaluated. Thermodynamic, kinetics and equilibrium studies were performed to assess the adsorption process. In addition, adsorption efficiency of adsorbents for treatment of a real textile wastewater as well as regeneration of prepared adsorbents after several times repetition of adsorption and desorption cycles were performed.

1.8 Organization of the thesis

The thesis is divided in to five major chapters and a section consists of references, appendix and publications. The first chapter represents an overview of the water pollution caused by industrialization. The effect of dyes on the environment, dyes wastewater treatment methods, adsorption and the use of chitosan as adsorbent are being discussed. Moreover, problem statement, research objectives, scope of study and organization of the thesis are presented in this chapter. Chapter two presents a detailed review of the related literature information on the chitosan

properties and use of chitosan and its derivatives for adsorption of different types of dye. This chapter also provides a detailed review on different modification techniques, environmental impacts and toxicity of chitosan modifications using different techniques. Finally, a literature review on the theory of adsorption process, isotherm models, kinetics and thermodynamic of batch adsorption process is presented.

Chapter three covers detailed information about the material and methods presented in this study. This chapter comprises all the materials and chemicals utilized during the experiments, preparation and modification procedures of adsorbents and their characterization techniques as well as description of various units of equipment used for the preparation, characterization of adsorbents and for batch adsorption and regeneration experiments. In addition, a summary of the research activities is briefly described in a flow sheet diagram.

Chapter four shows and elaborates in detail the all obtained results of the present investigation. The characterization of the unmodified and modified adsorbents used for adsorption experiments is presented in the first part. The next part represents the results and discussion for preparation and modification of adsorbents. The effect of adsorbent dosage, initial dye concentration, initial pH, time and temperature on adsorption of reactive dyes and reduction of COD through the batch adsorption process is discussed in detail in the next part. Furthermore, this part discusses the adsorption isotherms, kinetics and the thermodynamic studies. Moreover, desorption and regeneration results are presented and then comparison of the adsorption performance of the prepared adsorbents are discussed in this chapter.

Chapter five summarizes the important results obtained from this study and provided conclusions and recommendations for future research in the same area for the improvement of adsorption behavior of modified adsorbents. The last section of the thesis is consists of references, appendix and publications emanated from this research work.

CHAPTER TWO
LITERATURE REVIEW

This chapter consists of a detailed literature review of dye wastewater treatment methods aiming to highlight the adsorption of dyes on modified and unmodified chitosan. Some discussion on physically and chemically modifications of chitosan are presented. A review on the various parameters that affect the adsorption process is also included. Further, the theory of adsorption was presented in this section.

2.1 Water pollution

The increasing in world population, unplanned urbanization, industrialization, and agricultural activities, as well as the excessive use of chemicals have contributed to environmental pollution by producing high amounts of wastes and pollutants (Ahmad et al., 2007). Inorganic and organic wastes produced by human activities have resulted in high volumes of contaminated water, which leads to pollution of water sources and threatens human health and other living sources. Industries are identified as one of the major sources of water pollution by discharging untreated wastewater in waterways (Abdel-Aty et al., 2013).

Textile industries and other dyeing industries, such as paper, printing, leather, food, and plastic, are among the major industrial wastewater sources. Generally, the volume of discharged wastewater from each step of a textile operation is at as high as 40 L/kg to 65 L/kg of the product (Mezohegyi et al., 2012). The presence of dyes in textile wastewater is an environmental problem due to their high visibility,

resistance, and toxic impact (Ali et al., 2009). The presence of dyes even at low concentration in water is easily visible and can reduce photosynthetic activities in aquatic environments by preventing the penetration of light and oxygen. Therefore, biological cycles and photosynthetic activities affected and endangered (Crini, 2006). Given their synthetic origin and complex aromatic structures, dyes are non-biodegradable substances that remain stable under different conditions (Buthelezi et al., 2012). The half-life of hydrolyzed dyes can be very high. As an example the half-life duration of reactive blue 19 dye is approximately 46 years at 25 °C and pH 7 (Zaharia and Suteu, 2012). In addition, dyes have direct and indirect toxic effects on human in the form of cancer, jaundice, tumors, skin irritation, allergies, heart defects, and mutations (Alver and Metin, 2012; Hariharasuthan et al., 2013).

2.2 Dye wastewater treatment method

Environmentally, elimination of dyes from colored effluents is an important issue due to their negative impacts on the environment (even a small amount). Based on the governmental regulations, wastewater needs to be treated and thus, an effective process for removal of dyes is required (Lee et al., 2006). There are various methods that have been applied for the dyes wastewater treatment which are generally classified as physical, chemical, and biological (Ratnamala and Brajesh, 2013).

Biological wastewater treatment is the most common method for removing dyes from wastewater (Barragán et al., 2007; Frijters et al., 2006). In this method, bacteria are used to prepare the required energy for microbial activities through various wastewater components (Rai et al., 2005). This method is limited and

affected by factors such as dye concentration, temperature, and initial pH of the wastewater. Biological wastewater treatment is more environmental friendly, cost effective and appropriate for the removal of different dyes in comparision with other methods. However, this method also has drawbacks, including large area requirement, long decolorization time, and lack of flexibility in operation and design. In addition, this method might not be effective at low concentration (Mohammed et al., 2011; Crini, 2006).

Oxidation methods, ozonation, photochemical, irradiation or electrochemical processes are some chemical treatment methods. These methods are effective in eliminating dyes from wastewaters by using chemical reagents, such as aluminum, calcium, chlorine, lime, or ferric ions (Sabur et al., 2012). Disadvantages of these methods include large volume of sludge generated as waste, pH dependence, excessive chemical use and expensive reagents (Hassan et al., 2009). In Fenton process chemical reagent are used for treating waste waters. Chemical separation uses the action of sorption or bonding to remove dissolved dyes from textile. But one major disadvantage of this method is generation of sludge through the flocculation of the reagent and the dye molecules used in dyeing stage (Orta de Velsquez, 2002).

Physical methods for dye separation treatment process, include sedimentation, membrane, and adsorption, do not require any chemical reagent, bacteria, or microorganisms to improve the quality of wastewater (Ahmad et al., 2012; Gupta, 2009). Despite of the ability of these methods for dye removal from effluents as legal requirements, all of these methods are suffering from some limitations such as high cost or inability to remove wide range of dyes. Table 2.1 presents the advantages and disadvantages of various methods for dye treatment.

Table 2.1: Advantages and disadvantages of dye removal methods (Salleh et al. 2011)

Methods	Advantages	Disadvantages
Chemical treatments		
Oxidative process	Simplicity of application	(H_2O) agent needs to be activated by some means
H_2O_2 + Fe(II) salts (Fenton's reagent)	Fenton's reagent is a suitable chemical means	Sludge generation
Ozonation	Ozone can be applied in its gaseous state and does not increase the volume of wastewater and sludge	Short half-life (20 min)
Photochemical	No sludge is produced and foul odours are greatly reduced	Formation of by-products
Sodium hypochlorite (NaOCl)	Initiates and accelerates azo-bond cleavage	Release of aromatic amines
Electrochemical destruction	No consumption of chemicals and no sludge buildup	Relatively high flow rates cause a direct decrease in dye removal
Biological treatments		
Decolourisation by white-rot fungi	White-rot fungi are able to degrade dyes using enzymes	Enzyme production has also been shown to be unreliable

Table 2.1: Continued.

Methods	Advantages	Disadvantages
Other microbial cultures (mixed bacterial)	Decolorised in 24–30 h	Under aerobic conditions azo dyes are not readily metabolized
Adsorption by living/dead microbial biomass	Certain dyes have a particular affinity for binding with microbial species	Not effective for all dyes
Anaerobic textile–dye bioremediation systems	Allows azo and other water-soluble dyes to be decolorised	Anaerobic breakdown yields methane and hydrogen sulfide
Physical treatments		
Adsorption by activated carbon	Good removal of wide variety of dyes	Very expensive
Membrane filtration	Removes all dye types	Concentrated sludge production
Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Irradiation	Effective oxidation at lab scale	Requires a lot of dissolved O_2
Electrokinetic coagulation	Economically feasible	High sludge production

2.3 Adsorption

Adsorption is a simple and effective process for dye removal from wastewater. This treatment method is attractive for effluents if low-cost adsorbents can be used. The application of the adsorption in the early days is not clear. However, there are some information available on some applications such as the use of some special materials to decolorize some solutions. In addition, the first use of adsorption process in large scale is reported to be in the early 1920 in Germany and United States (King, 1987). Over the past few decades, application of adsorption, has gained more importance in the industry and has been further developed for environmental protection.

Among water treatment strategies, adsorption is regarded to be an effective and preferable method for removing dyes from wastewater. This method is rapid, convenient, cost effective as well as requiring low initial costs, simplicity of design and operation, nontoxic by-products while producing high-quality effluent (Oluyemi et al., 2012). Adsorption is a separation process, in which the amount of chemical components (adsorbate) being collected, concentrated and retained at the surface of a solid (adsorbent) (Yadla et al., 2012). This process incorporates both physical and chemical actions that involve van der Waals forces, or other actions between an adsorbate and an adsorbent (Wang et al., 2009).

Adsorption efficiency is affected by the nature and type of adsorbent. An ideal adsorbent for dye removal possesses the following properties: large surface area and adsorption capacity, sufficient pore size and volume, easy accessibility, cost effectiveness, mechanical stability, compatibility, ease of regeneration, and high selectivity to remove a wide range of dyes (Egashira et al., 2012; Najafi et al., 2011).

Both organic and inorganic materials can be used as adsorbents for dye removal. Researchers have focused on activated carbon (Ribas et al., 2014), alumina (Shen et al., 2015), zeolites (Liu et al., 2014), silica gel (Wang et al., 2014), industrial by-products (Hameed et al., 2009), agricultural solid wastes (Bharathi and Ramesh, 2013), clays (Abidi et al., 2015), peat (Rovani et al., 2014), bacterial biomass (Przystaś et al., 2012), and polysaccharides (Gao et al., 2015).

Activated alumina is synthesized by the thermal treatment of hydrous alumina granules. Specifically, thermal treatment removes hydroxyl groups, thereby leaving a porous solid structure of activated alumina with a large surface area of 200 m^2/g to 300 m^2/g. The adequate surface area of activated alumina makes it an appropriate adsorbent to remove pollutants from aqueous solutions. Previous studies have evaluated the capacity of activated alumina to remove dyes (Adak et al., 2005; Adak et al., 2006; Huang et al., 2007). Zeolites are hydrated aluminosilicate minerals with a porous structure. They are naturally formed through changes in glass-rich volcanic rocks (tuff) by sea or playa lake water. Zeolites can also be synthesized and are considered as appropriate adsorbents for removing pollutants from wastewaters. The good adsorption behavior is due to their effective properties, including high ion exchange, and their applications in molecular sieving, catalysis, and sorption (Ji et al., 2012; Wang and Peng, 2010). Some zeolites can be used for the removal of dyes (Alpat et al., 2008; Yu et al., 2013) and other pollutants, such as heavy metals (Malamis and Katsou, 2013; Šljivić Ivanović et al., 2013). Silica gel is a concentration of $Si(OH)_4$ in siloxane chains and was invested in the 1920s. Silica gels could be present in the form of regular, intermediate, or low density with a surface area of 750 m^2/g, 300 m^2/g to 350 m^2/g, and 100 m^2/g to 200 m^2/g. Silica gel

is a suitable adsorbent because of its valuable physicochemical properties, such as stability under acidic conditions, rapid adsorption, and porous structure with high surface area. Although it is also nontoxic, nonflammable, and chemically ineffective, the use of silica gel is limited due to its high cost (Salam et al., 2011; Fan et al., 2011). Gaikwad and Misal (2010) and Samiey and Toosi (2010) have reported the use of silica gel for dye adsorption.

Activated carbon, with an outstanding capacity to adsorb various chemicals, is one of the oldest and important adsorbents utilized for wastewater treatment worldwide (Salleh et al., 2011). Carbon is activated through dehydration and carbonization in the presence of heat and in the absence of oxygen. The produced activated carbon has an amorphous structure with small pores and a large surface area of 300 m^2/g to 4000 m^2/g. Although activated carbon is an effective adsorbent for eliminating different dyes, it is still limited by its high cost and requirement of regeneration after adsorption, which leads to decreased adsorption capability and increased cost (Bhatnagar and Minocha, 2009). In general, a good adsorbent should be cost effective, readily available, environmentally friendly, and does not require heavy processing and maintenance. Hence, researchers have focused on developing materials based on natural polymers such as chitosan to serve as alternative adsorbents with improved adsorption capacity and low cost (Wan Ngah and Hanafiah, 2008).

2.4 Chitosan

Chitosan is one of the world's most plentiful and low-cost biopolymers that possess several suitable properties to be used as an ideal adsorbent for removing

pollutants from wastewater. Originally, chitin was boiled in potassium hydroxide to produce an acid-soluble product called chitosan (Kavitha et al., 2011). Chitin, the second most abundant polysaccharide worldwide can be extracted from fungal species or from the exoskeleton of sea creatures such as crayfish, lobster, prawns, crab and shrimp (Gavhane et al., 2013). Figure 2.1 shows the molecular structure of chitosan. Chitosan or poly-(1,4)-2-amino-2-deoxy-b-D-glucose is a biopolymer that can be chemically expressed as nontoxic, heterogeneous, linear, cationic and biodegradable polysaccharide with high molecular weight (Riva et al., 2011). Chitosan is produced from the alkaline de-acetylation of chitin (Hsiao et al., 2013). In this process, the acetyl groups of chitin are hydrolyzed and converted to free amine groups. This step determines the degree of de-acetylation (DD) or the ratio of de-acetylated to acetylated units.

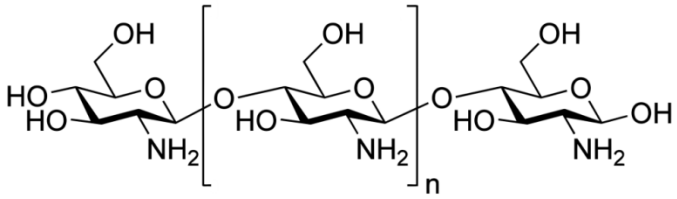


Figure 2.1: Molecular structure of chitosan.

DD is influenced by temperature, time and the concentration of sodium hydroxide used in the de-acetylation (Hsiao et al., 2013; Hussain et al., 2013). The degree of de-acetylation affects the adsorption capacity of the chitosan. High DD generally results from the presence of high amounts of amino groups and it can increase dye adsorption capacity of the chitosan by protonation (Piccin et al., 2009). DD is commonly used to characterize chitosan alongside other properties such as

molecular weight, crystallinity, and distribution of amine groups which determine the physicochemical, biological and reaction of chitosan in the solution (Jana et al., 2013; Sorlier et al., 2001). Previous studies reported that molecular weight affects the solubility (solubility decreases with increasing molecular weight), tensile strength (Park et al., 2002), bacteriological properties (Cárdenas et al., 2008), coagulant-flocculant performance of chitosan (Aranaz et al., 2009) and crystallinity (Jaworska et al., 2003). Meanwhile, crystallinity affects the adsorption capacity (Piron et al., 1997) and accessibility of amine groups (Guibal, 2004).

Chitosan is insoluble in water, alkaline solutions and organic solvents because of the hydrogen bonds between its molecules. However, it is soluble in acidic solutions due to the protonation of its amine groups (Aranaz et al., 2009; Hamdine et al., 2005). Based on the above properties chitosan potentially has high affinity to adsorb pollutions such as heavy metals (Ren et al., 2013) and dyes (Peng et al., 2013). However, some drawbacks such as solubility in acid and low surface area limit the performance of this material in the adsorption process. This necessitated the modification of chitosan for dye removal by many researchers as elaborated in the following sections.

2.5 Unmodified chitosan

Many researchers have investigated the adsorption performance of different forms of chitosan. The obtained chitosan from chitin; a solid material with high crystallinity called chitosan flakes, has been used by a few researchers as an adsorbent for dye removal from aqueous solutions. Piccin et al. (2009) prepared chitosan from shrimp waste and used to eliminate food dyes (FD&C Red No. 40)